zhou City, China. *Proc Spie*, 8286(4), p.p.393-403.

15. Hu J, Shi X, Song J, et al. (2005) Optimal Design for Urban Mass Transit Network Based on Evolutionary Algorithms. *Proceedings of the First international conference on Advances in Natural Computation - Volume Part IISpringer-Verlag*, p.p.1089-1100.
16. Liu X P, Xia L I, Yeh G O, et al. (2007) Discovery of transition rules for geographical cellular automata by using ant colony optimization. *Science in China*, 50(10), p.p.1578-1588.
17. Gao Y, Yang H R. (2011) Study on Planning of Urban Infrastructure Based on Ecologized Landscape Design. *Procedia Engineering*, p.p.498–503.

Influence of the Surfactant on the Coupling Force between the Object Surface and the Particles

Wu Guixiang

School of Resources and Safety Engineering, Central South University, Changsha 410083, Hunan, China

Abstract

Based on the DOLV theory about the coupling and expansion between the object surface and the particles, this paper studies the influence of the addition of surfactants on the deviation of particles from the object surface, and establishes a relevant mechanical expression. The addition of the surfactant reduces the Van Der Waals force, double electrode layer acting force and hydrated force between the object surface and the particles to separate particles. The parameters with a greater influence include Hamaker constant, Debye length, object's surface potential and ion strength, density, dielectric constant and polarizability of the electrolyte in the solution and so on. The experiment result of the acting force between the object surface and the particles measured through the ultrasonic vibration shows that: Under the influence of no external force, the removal rate of the surfactant solution of the blots is five times as much as that of the distilled water. In other words, the acting force F(h) 1between the particles and the object surface (in the surfactant solution)<F(h) 2 (in the distilled water). The effect and the removal rate of the anionic surfactant and the nonionic surfactant are different, but can all change the physical characteristics of the adherent particles, making blots on the glass surface easier to be removed.

Key words: SURFACTANT, HAMAKER CONTANT, ELECTRIC DOUBLE LAYER, HYDRATION FORCE, PARTICLE

1. Introduction

Parent groups of surfactant are distributed directionally in liquid/solid, liquid/liquid and solid/solid interface. When polar groups are combined with the object surface, polar water molecules or hydrophilic groups will occupy the particulate surface and change the nature of solid surface, detaching particles from the surface.

As surfactant has special surface-active properties, it is widely used in environmental protection, food, hygiene, metallurgy, medicine and other fields[1-3]. Existing research has reported a lot on the composition and structure of surfactant and its adhesive mechanism on object surface[4-5].

However, few studies have been reported on how surfactant detaches particles from object surface. Based on the adhesion science between particles, this paper discusses how surfactant reduces the interaction between particles and object surface and further enriches the basic theory on particulate removal with surfactant. This paper also has a certain guiding significance for the selection of detergent or eco-friendly reagent.

2. A Mechanical Analysis of the Effect of Surfactant on the Interaction between Object Surface and Particles

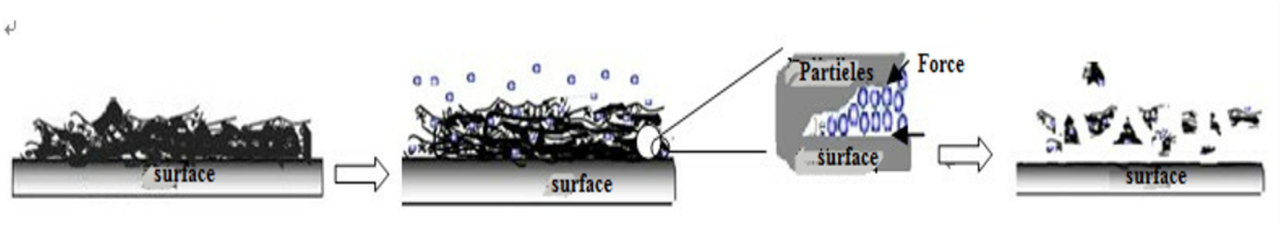
2.1. The removal mechanism of particles on object surface with surfactant

Particles adhere to object surface mainly by Van der Waals' force (F_{adh}),electrostatic force (F_E),capillary force (F_e) and chemical force (F_c). The total interaction between them is:

$$F(h) = F_{adh} + F_E + F_e + F_c \qquad (1)$$

Where F_{adh} is a universal force. F_c is the magnitude. If F_c is large, the adhesion of particles is generally secure. But it is not universal. F_e is the force pulling particles towards the surface, inside the crack between two contacted objects, as a result of humid air. F_E is caused by electrostatic attraction between particles and substance surface, due to the charging of particles or static electricity from outside.

The adhesion of particles on object surface is complex. They don't spread like liquid. Fig. 1 shows micro cracks (i.e. capillaries) in solid-solid interface adhered in the form of point and surface. If water is used as a wetting agent, due to high surface energy, it may not be favorable for infiltration process. After infiltrating into micro cracks, the interaction between object surface and particles seldom deceases. It cannot reduce the interaction between particles and object surface effectively. When adding water-soluble surfactant as shown in Fig. 1b,surfactant adsorbs directionally in water-solid interface, depending on ionic exchange adsorption, ionic para-adsorption, hydrophobic attraction adsorption, dispersion force adsorption and π electronic polarization, etc., which reduces the surface free energy of water and increases capillary force. This is favorable for the infiltration of surfactant solution into micro cracks. When surfactant infiltrates into micro cracks, hydrophobic groups of surfactant will adhere to solid surface and particles. The hydrophilic groups in it will stretch into the solution, changes the nature of solid dirt and object surface, changes the interaction between particles and object surface, making the stress of particles along the contact line unbalanced. Whether particles can be detached from object surface depends on F(h),the solid-solid interaction[6]. If F(h)< 0,the repulsion between particles and object surface is greater than their attraction. Particles are thus detached from object surface. If F(h)> 0,particles and object surface attract each other. The addition of surfactant makes the gathered particles loose and detached from object surface under the effect of mechanical force, as shown in Fig. 1c.



a. Particles are adhered to the object surface b. The infiltration of surfactant c. Particles are detached from the object surface

Figure 1. The schematic diagram of particle detached from the object surface

2.2. Mathematical expressions for the Effect of Surfactant on the Interaction between Particles and Object Surface

Classic DLVO theory presents methods to calculate mutual attraction energy and double electrode layer repulsion energy between various shapes of particles under different circumstances. It argues that interaction between particles is mainly composed of Van der Waals' force and electrostatic force. In a certain distance, Van der Waals' force between solid surface and solid dirt is often attractive, while the electrostatic force of double electrode layer is mainly repulsive. The addition of surfactant complicates the interaction between object surfaces and particles. Apart from Van der Waals' force and electrostatic force variation included in classic DLVO theory, the hydration force between hydrophilic groups is also added.

2.2.1. Van der Waals' force

2.2. 1.1 Van der Waals' force between particles and object surface

Van der Waals' force is a type of universal force and produced by atomic nucleus in an atom attracting peripheral electrons in another atom. Van der Waals' force is found between molecules. It is a key factor for particles to be adhered to object surface. Van der Waals' force between thick plates of two different natures is shown below:

$$F_{adh} = \frac{A}{6\pi h^3} \tag{2}$$

Where A is the Hamaker constant of object surface and particles in water. The value of A is determined by the chemical properties of particles, object surface and disperse medium between them. Alex Nikolov[7] listed the dielectric constant, refractive index and absorption frequency of some substances,for example, water=80F/m, $\nu_e=3\times10^{15}$Hz,n=1.333. The biggest influencing factor of Van der Waals' force between objects is Hamaker constant. If the distance between particles and object surface h remains unchanged, the number and symbol variation of A determines the magnitude of Van der Waals' force and whether particles and he object surface are attractive or repulsive.

2.2. 1.2 The effect of surfactant on Van der Waals' force

The molecular structure of surfactant in water solution is asymmetric and polar. Molecules contain both hydrophilic groups and oleophylic groups. Hydrophilic groups often include carboxyl, sulphonate, ether, chlorine and hydroxyl groups, etc. Oleophylic groups often include hydroxyl groups. Generally, ● stands for hydrophilic groups and-stands for oleophylic groups. Surfactant forms an adsorption layer on solid surface and solid dirt, as shown in Fig. 2 below. h is the thickness of different functional groups (e.g. carboxyl). d is the distance between two surfaces after adsorbing surfactant [8].

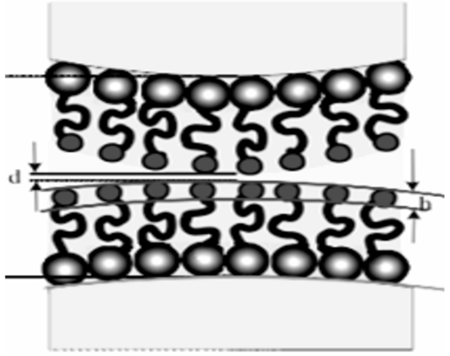


Figure 2. The schematic diagram of surfactant adsorption

In the absence of surfactant, Van der Waals' force between object surface and particles is relative simple. After adsorbing surfactant, Van der Waals' force between solid surface and solid dirt becomes complicated. Their interaction is as follows:

$$F_{adh} = F_{bulk} + F_{thin} \tag{3}$$

F_{bulk} is Van der Waals' force energy between two planes in the absence of surfactant absorption. F_{thin} is Van der Waals' force energy between thin surfactant layers:

$$F_{thin} = \frac{A}{6\pi}\left(\frac{1}{(h+d)^3} - \frac{1}{(2h+d)}\right) \tag{4}$$

Where the Hamaker constant of surfactant in water is:

$$A_{12} = \frac{3}{4}KT\left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \times \frac{(n_1^2-n_2^2)^2}{(n_1^2+n_2^2)^{3/2}} \tag{5}$$

Where k is Boltzmann's constant,1.38x10^{-23}J/K,ε_i is the dielectric constant of all substances, n_i is the refractive index of all substances, h is the Planck constant,6.626176$\times$10^{-34},and ν_e is the absorption frequency of substances. The effect of dielectric constant on Van der Waals constant is smaller than that of refractive index. If it only accounts for about 1% in the non-polar solution, Formula (5) is approximate to Formula (6)

$$A_{12} = \frac{3h\nu_e}{16\sqrt{2}} \times \frac{(n_1^2-n_2^2)^2}{(n_1^2+n_2^2)^{3/2}} \tag{6}$$

The refractive index of surfactant n is associated with oleophylic groups (e.g., CH = CH functional groups),hydrophilic groups (e.g., carboxyl functional groups) and structure of surfactant.

Taking only oleophylic groups of surfactant into account, the refractive index n (j,0) can be represented as:

$$n\text{-}1 = \rho\left(\frac{\kappa}{\rho_{ref}}\right) \tag{7}$$

Where κ/ρ_ref is a constant. The refractive index of surfactant n and the density ρ increases with the number of carbon atoms j in oleophylic groups, j. But n-1/ρ decrease with the increase of the number of carbon atoms j in oleophylic groups.

The effect of hydrophilic groups (e.g. carboxyl functional groups) can be represented as:

$$\Delta n \approx j[n(j,1)\text{-}n(j,0)] \tag{8}$$

Where n(j,1) is the refractive index of surfactant. For the same kind of hydrophilic functional groups, Δn is always constant and doesn't change with the number of carbon atoms in hydroxyl groups.

2.2.2 Electrostatic force

After solid particles and object surface are soaked in water, some substances on their surface are dissolved by water and diffuse in it. Among them, cations diffuse faster than anions, thus anionic concentration in particles or object surface is higher than cationic concentration and forms a negative electrode layer. Therefore, due to repulsion between the same kind of charges in particulate particles and fabric surface, the adhesion strength between particles and fabric surface will be weakened in water. Due to ionic diffusion and adsorption in solid particles or object surface, a double electrode layer will be formed. When the distance between solid particles and object surface is close enough, mobile ions in diffusion layer of double electrode layer will overlap and produce an electrostatic interaction. The surface potential formed by the ionization of solid particles in water is low. D. Manev held that the electrostatic force was [9] :

$$F_E = \frac{\varepsilon\varepsilon_0\kappa^2\varphi^2}{\cosh(\kappa h)\pm 1} \tag{9}$$

Where φ is a thermodynamic unit of object surface. κ^{-1} is the length of Debye, which stands for the thickness of double electrode layer.

$$\kappa^{-1} = \left(\frac{1000\varepsilon KT}{8\pi e^2 N_A I}\right)^{1/2}.$$

ε is the absolute constant of disperse medium. ε_{water}=78.5. N_A is the Avogadro constant, 6.022×10^{23} mol^{-1} and I is the ionic strength[10].

The removal of particles is mainly fulfilled by mutual repulsion between double electrode layers and mechanical force of system. After surfactant is adhered to particles and object surface, their surface nature changes a lot. The electrolyte concentration changes, too. The superimposed surface potential is high. With the addition of anionic surfactant, when active anions are adhered to particulate particles and object surface, the negative surface potential between them will increase, that is, the potential of stern layer will be increased and enhance the electrostatic repulsion between them. The adhesion strength of particles becomes lower. Particles are easier to remove. Due to the adsorption of cationic surfactant to particles and substances, the original surface potential will be reduced or eliminated, making electrostatic repulsion between particles and object surface decrease or disappear. So it is unfavorable for the removal of particles. The addition of carboxyl and methyl fiber macromolecules also forms electric energy barriers in particles and on substance surface. The electrostatic force can be represented with the following formula[11]:

$$F_E \approx 64KTn_0\gamma^2e^{-\kappa h} \tag{10}$$

Where in $\gamma = \tanh\left(\frac{ze\varphi}{2KT}\right)$, *z* is the ionic valence, *e* is the electronic charge and n_o is the electrolyte concentration in solution. From Formula (10),it can be seen that a greater influencing factor on electrostatic force is object surface potential φ. The object surface potential $\varphi$is derived from γ. When φ is small, it has a great impact on electrostatic force. When φ increases to a certain value,$\gamma \approx 1$ and it is less affected byφ. Fig. 3 in Reference [12] shows the kaolin surface potential variation in different types of SAA. It can be seen that when object surface absorbs cationic surface activity, the kaolin surface potential will increase a lot, while anionic surfactant is just the opposite. The non-ionic surface activity φ doesn't change a lot. Κ includes the effect on electrolyte concentration in solution. The effect of anionic surfactant concentration on the reciprocal of double electrode layer thickness Κ increases with the concentration of solution[13].

2.2.3. Hydration force

When object surface absorbs hydrophilic cations (e.g., Ca^+) or surfactant containing hydrophilic groups (—OH,—$CONH_2$),it will form a hydration layer on the hydrophilic surface. Cations (e.g. Ca+) or hydrophilic groups (—OH,—$CONH_2$) will penetrate the hydration layer on the surface. When two surfaces get close, they will produce a strong hydration repulsion, i.e., two hydration layers containing hydrophilic groups will produce repulsion through space, i.e. hydration repulsion, whose magnitude depends on energy required to destruct the orderly structure of water molecules and dehydrate adhered cations or hydrophilic groups[14-15]. The group distance within which it works is smaller than electrical repulsion. With the same kind of charges, ionic surfactant produces electrical repulsion. Non-ionic surfactant molecules don't have Coulomb repulsion, but primarily hydration force. The hydration force is shown in the following formula [16]:

$$F_{HR} = K\exp(-\frac{h}{\lambda}) \tag{11}$$

Where λ is the attenuation distance constant. When electrolyte in the solution is 1:1 electrolyte,$\lambda \approx 0.6\text{-}1.1$nm, $K = 2\varepsilon_0 P_0^2/a_0$[17]. ε_0 is the dielectric constant. P_0 is the object surface polarization,a_0 is the polarizability of solution and K often varies within 3-30mJ/m²[18].

3.Experimental Research

3.1. Experimental methods and procedures

100mm × 50 mm × 3 mm slides were chosen as substrates. Slides No. A_{1-3} were soaked in LAS (sodium dodecyl benzene sulfonate,SDBS) diluted by 1/1000,retained for a moment and then lifted smoothly uniformly and vertically. A1-3,together with Slides No. B1-3 rinsed with distilled water, was dried in a thermostat for 20 min at 80 °C. 6 dried slides were placed flatwise on an experiment table in the middle of a lab and set aside for 30d. Dust-detained slides were put under a microscope. Peripheral area along the centerline was selected as the observation object. The observation area was analyzed with a microscopic image analysis system. The number, maximum diameter and average diameter of particles in the selected area were analyzed. After analysis, slides were fixed on the rim of a beaker filled with some water, oscillated for 2 min in an ultrasonic oscillation instrument and then analyzed again with the microscopic image analysis system. The number of particles was compared with results in previous analysis, to calculate the average removal rate of particles in uncoated ultrasonic oscillation and coated ultrasonic oscillation.

After Slides No. C_{1-6},D_{1-6} and E_{1-6} were attached under a kitchen exhaust fan with adhesive tape for 20d,they were dried in a drying oven for 8h at 80 °C,-set aside in a dry dish for 30 min and weighed with a balance. Slides No. $C_{1-}6$ were soaked in distilled water for 15 min. Slides No. D_{1-6} and E_{1-6} were soaked in LAS and Tween 80 diluted by 1/100 for 15 min. After soak, Slides No. C_{1-3},D_{1-3} and E_{1-3} were taken out and weighed. After ultrasonic oscillated for 2 min, Slides No. C_{4-6},D_{4-6} and E_{4-6} were taken out, dried and weighed. The average removal rate of kitchen stains on glass surface after distilled water soak, LAS soak, Tween 80 soak, distilled water soak+ ultrasonic oscillation, LAS soak+ ultrasonic oscillation, Tween 80 soak+ ultrasonic oscillation was calculated.

3.2. Experimental results and discussion

Ultrasonic oscillation separation technology can be used to measure the interaction between particles and object surface. The mechanism is as follows: add sinusoidal oscillation acceleration to a direction perpendicular to the object surface. Particles are detached from object surface under the effect of inertia. The adhesion strength between particles and object surface is judged by measuring particles detached from object surface. Fig. 3 is the removal rate of particles on glass surface in different modes (Fig. 1~8 are distilled water soak, LAS soak, Tween 80 soak, distilled water soak+ ultrasonic oscillation, LAS soak+ ultrasonic oscillation, Tween 80 soak+ ultrasonic oscillation, uncoated ultrasonic oscillation and coated ultrasonic oscillation respectively). When an ultrasonic oscillation instrument is started, due to oscillation, a drag force F_D is produced around the particles. When $F_D > \mu F(h)$,particles are detached from object surface. F_D is a constant value. If the removal rate on object surface is high, it suggests that the interaction between particles and object surface is small. The removal rate of particles on No. "7" uncoated glass surface is 34.67%,which is less than 45.84%,the removal rate of particles on No. "8" detergent-coated glass surface. The addition of surfactant reduces the interaction between particles and glass. From Reference [19],it can be learned that with a small particle size, the interaction between particles and glass in dry environment is mainly Van der Waals' force. So the addition of surfactant can effectively reduce Van der Waals' force between glass and atmospheric particles.

Changing the structure of surfactant will affect the Hamaker constant between particles and object surface and cause Van der Waals' force between particles and object surface to change. Particles will be detached from object surface automatically or under the effect of mechanical force. Since water is added to No."1~6",the medium between dirt and glass surface change into water or surfactant solution. The interaction between dirt and glass surface will change. Anionic surfactant increases F_E, the electrostatic repulsion between particles and object surface, by changing the surface potential of double electrode layer and the length of Debye. Non-ionic surfactant mainly changes the nature of particles and object surface, to produce a strong hydration force, F_{HR}. In this way, surfactant increases electrostatic repulsion and hydration force between kitchen stains and glass surface.

The removal rate of particles on No. "1" glass surface is lower than that of No. "2" and "3". The removal rate of particles on No. "4" glass surface is lower than that of No. "5" and "6". In the absence of external force, the removal rate of stains with surfactant solution is 5 times that of distilled water. The addition of ultrasonic oscillation force makes it easier for surfactant to remove dirt. The removal rate reaches 93.1%. Fig. 4 is the diameter variation of particles pre and post ultrasonic oscillation (Fig.1~4 are uncoated, detergent-coated, ultrasonic oscillation and SDBS-coated+ ultrasonic oscillation respectively). It can be seen that the maximum diameter and average diameter of particles on glass surface are affected by surface coating. The adhesion strength of SDBS is larger than uncoated conditions. Particles are dispersed under the effect of oscillation. The maximum diameter and average diameter of No. "3"and "4"are greater than those of No. "1"and "2".

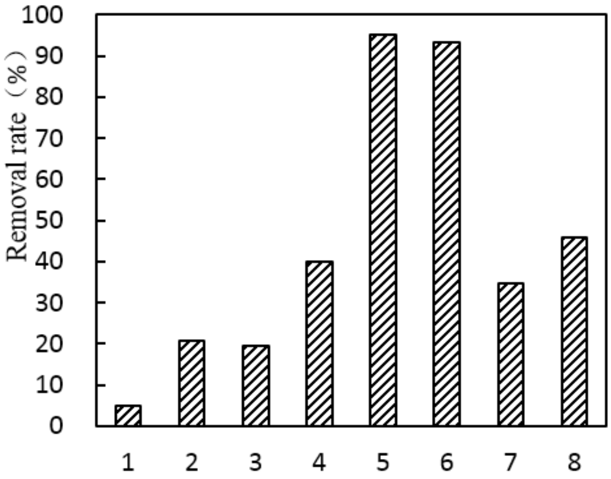


Figure 3. The removal rate of partical on glass

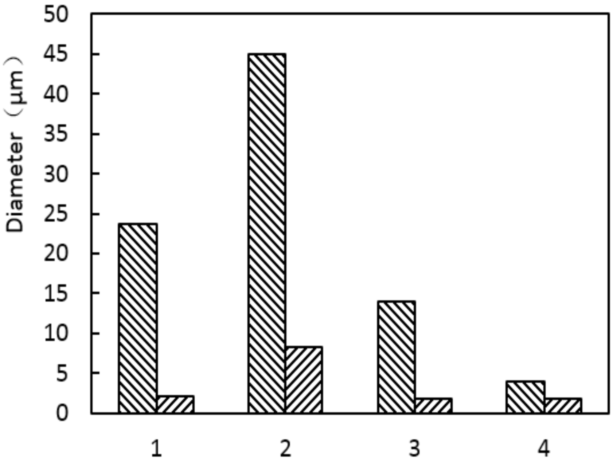


Figure 4. The diameter variation of particle on the glass surface pre and post ultrasonic oscillation

4. Conclusion

(1) Surfactant adsorbs directionally in water-solid interface, depending on ionic exchange adsorption, ionic para-adsorption, hydrophobic attraction adsorption, dispersion force adsorption and π electronic polarization, etc.

(2) Surfactant makes particles loose or detached from object surface, by reducing Van der Waals' force between particles or object surfaces and increasing the electrostatic repulsion and hydration force of double electrode layer between them. Besides, different natures of surfactant play different roles in removing surface particles and set up a mechanical model for the effect of surfactant on the interaction between object surface and particles.

(3) Compared with uncoated glass surface, with ultrasonic oscillation separation technology, particles are more likely to be detached from surfactant-coated glass surface, because surfactant reduces Hamaker interaction between particles and glass surface by reducing Hamaker constant. Compared with cleaning experiments of stains on glass surface with distilled water, SDBS soak and Tween 80 soak, either soak or ultrasonic oscillation, surfactant has a higher removal rate of oil stains than distilled water, which verifies mathematical expressions proving that surfactant can effectively reduce the interaction between object surface and particles.

References

1. Huang Z.L,Chen Q Y.(2014) Comparison the Effect of Washing Diesel Oil-contaminatesoil By Five Kinds of Surfactants. *Environmental Engineering*,6(1), p.p.168-172.
2. Huang S.C, Liu X,Ye S. E, Liu X. Q. (2014) Improvement of Silicon Wafer Wet Chemical Cleaning Process by Adding Surfactant and Chelating Agent. *Semiconductor Optoelectronics*, 35(3) , p.p.468-474.
3. Che W. C, Dong L,Chen S. F. (2014) Study on detergency of surfactant ethoxylated rosin ester. *China Surfactant Detergent & Cosmetics,*44(8), p.p.439-442.
4. Wu G.X,Wu C, Peng X.L. (2005) Mechanism of adhesion and cleaning between the surface of structural glass and dust. *Journal of Safety Science and Technology*,1(5), p.p.26-30.
5. S.M. Mirabedini,A. Kiamanesh (2013) Modelling of spontaneous adhesion phenomena in micro-electro-mechanical systems. *European Journal of Mechanics*, 39(5), p.p.144-152
6. P.G.C. P,M.L. A.(2015) Determining the adhesion force between particles and rough surfaces . *Powder Technology*, 274, p.p.67–76.
7. Alex N, Darsh W. (2014) Wetting–dewetting films: The role of structural forces. *Advances in Colloid and Interface Science* , 206(2), p.p. 207-221.
8. Preeti S.Y,Derek D,Rafael T. (2007) Effective refractive index and intermolecular forces associated with a phase of functional groups.

Surface science, 601, p.p.4582–4585.

9. Anh V. N . (2005) Effects of surfactant adsorption and surface forces on thinning and rupture of foam liquid films. *Mineral Processing*,77(1) , p.p. 1-45.
10. Liu, D., A.M. Pourrahimi,Olsson R.T. (2015) Influence of nanoparticle surface treatment on particle dispersion and interfacial adhesion in-low-density polyethylene aluminium oxide nanocomposites. *European Polymer Journal*, 40, p.p.6667–77.
11. Kar, G.,Chander.S, Mika T.S . (1973) The potential energy of interaction between dis-similar electrical double layers. *Colloid Interface Sci*, 44 (2) , p.p. 347–355.
12. Abdin K,Y.(2005) Zeta potential of soils with surfactants and its relevance to electrokinetic remediation. *Hazardous Materials*, 120(1-3), p.p.119-126.
13. Emil D.M,Aah V.N. (2005) Effects of surfactant adsorption and surface forces on thinning and rupture of foam liquid films. *Miner process*,77(1), p.p.1-45.
14. Parsegian V.A, Zemb.T. (2011) Hydration forces: Observations, explanations, expectations, questions. *Current Opinion in Colloid & Interface Science*, 16, p.p.618–624.
15. Churaev N.V. (2003) Surface in wetting films. *Advances in colloid and interface science*, 103, p.p. 197-218.
16. Arasons,D F. Ninham B.W.(2011) Surface charge reversal and hydration forces explained by ionic dispersion forces and surface hydration. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 383, p.p.2–9.
17. Bostrom. M, Williams. D. R. M,Ninham. B.W. (2011) Ion Specificity of Micelles Explained by Ionic Dispersion Forces. *Langmuir*, 18(16) p.p. 6010-6014
18. Kralchevsky P A.,Krassimir D. D.(2011) Hydration force due to the reduced screening of the electrostatic repulsion in few-nanometer-thick films. *Current Opinion in Colloid & Interface Science*, 16(6) , p.p. 517-524.
19. Li Y.Q,Wu C. (2007) Visual Research on the Mechanical Models of Micro-particle Adhesion on the Surface. *Safety and Environmental Engineering*, 14(3) , p.p.15-18.